

Attorney Docket No. MSU 4.1-643
Appln. Serial No. 10/691,328
Amendment dated January 3, 2007
Reply to Office Action dated August 15, 2006

REMARKS

Claims 1 to 46 are pending. Claims 1 to 15, 17, 18, 21, 22, 24 to 43, 45 and 46 were allowed.

Claims 16 and 44 were rejected based upon noted errors in the claims. The claims have been corrected.

Claims 19, 20 and 23 were rejected under 35 USC 102(a) as being anticipated by Ciszewski et al. "Synthesis and structure of an imido-ethered Schrock carbene of molybdenum", Dalton Trans., 2003, pages 4226-4227. This publication is less than one (1) year from the filing date of the application and is a publication by the inventors, James T. Ciszewski and Aaron L. Odom. Enclosed is the Disclaimer of Inventorship from Changsheng Cao. The other author Baohan Xie may be added as an inventor and this is being determined now. Reconsideration is requested.

Attorney Docket No. MSU 4.1-643
Appln. Serial No. 10/691,328
Amendment dated January 3, 2007
Reply to Office Action dated August 15, 2006

It is now believed that Claims 1 to 46 are in
condition for allowance. Notice of Allowance is
requested.

Respectfully,



Ian C. McLeod
Registration No. 20,931

IAN C. McLEOD, P.C.
2190 Commons Parkway
Okemos, Michigan 48864

Telephone: (517) 347-4100
Facsimile: (517) 347-4103
Email: ianmclcd@comcast.net

Enclosure: Disclaimer of Inventorship by
Changsheng Cao

Synthesis and structure of an imido-tethered Schrock carbene of molybdenum†

James T. Ciszewski, Baohan Xie, Changsheng Cao and Aaron L. Odom*

Department of Chemistry, Michigan State University, East Lansing, MI, USA.

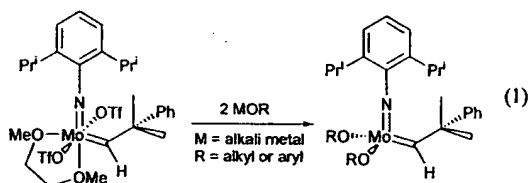
E-mail: odom@cem.msu.edu

Received 16th September 2003, Accepted 16th September 2003

First published as an Advance Article on the web 25th September 2003

An 8-membered molybdenum azametallacycle, where a Mo=C bond and a Mo=N bond are linked, incorporating two triflate co-ligands has been synthesized and structurally characterized.

Metal-carbon double bonds where the metal is in a moderate to high oxidation state, Schrock carbenes or alkylidenes, seem to have an ever-increasing importance in small molecule and polymer chemistry due to their activity in double-bond metathesis.^{1,2} Since the original discovery of high oxidation state carbenes by Schrock in 1973,³ a plethora of carbene complexes in moderate to high oxidation states have been prepared across much of the periodic table.⁴ Some of the most active double-bond metathesis catalysts are the molybdenum(vi) imido carbene complexes, which are prepared by addition of alkoxides to bis(triflate) precursors (Equation 1). The triflate ligands may be replaced by a variety of different alkoxides,⁵ including chiral ancillaries⁶ for use in enantioselective ring-closing metathesis and solid-supported alkoxides.⁷



Fürstner and co-workers provided the initial reports on tethering the reactive ruthenium carbene functional group to an *N*-heterocyclic carbene ancillary ligand (Fig. 1).⁸ These carbenes were investigated for ring-closing metathesis as catalysts capable of regenerating the original species on depletion of substrate. More recently, Grubbs and coworkers have examined tethered ruthenium carbenes for selective cyclopolymerization of olefins by ring-opening metathesis polymerization.⁹ The tether retains a high local concentration of both termini of the growing polymer near the metal, enabling a final macrocyclic ring-closing metathesis event.

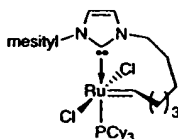


Fig. 1 Ruthenium catalyst with carbene tethered to ancillary ligand.

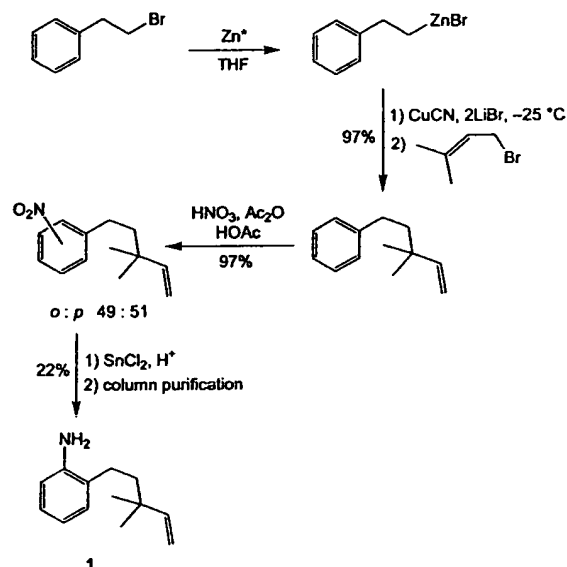
In a similar vein, we have been investigating the chemistry of tethered molybdenum carbenes, where the active carbene centre is attached through an aliphatic chain to an ancillary ligand on molybdenum. Like its ruthenium counterparts, it is hoped that

† Electronic supplementary information (ESI) available: Synthetic details for the generation of 2-(3,3-dimethylpent-4-enyl)aniline (1) and the tethered molybdenum carbene 4. Tables for the X-ray diffraction study on 4. See <http://www.rsc.org/suppdata/dt/b3/b311320p/>

tethered catalysts would provide greater catalyst reusability by trapping less stable methyldiene intermediates once substrates are consumed. In addition, cyclo-oligomerization and -polymerization products with numerous possible applications may be accessible utilizing these new molybdenum complexes.

To generate a stable tethered carbene and provide a bis(triflate) precursor useful for a variety of purposes, it was desirable to use the imido substituent as the ancillary ligand of attachment. However, relatively few complexes are known where two molybdenum metal-ligand multiple bonds are tethered to form a metallacycle. A few Group-6 mutually tethered di-carbenes have been reported, usually prepared through oligomerization of alkynes by reduced complexes.¹⁰ Tethered Group-6 bis-(imido), *ansa*-di(organoimido), complexes have been prepared as analogs of *ansa*-metallocenes of the Group-4 elements and studied for Zeigler-Natta polymerization activity.¹¹ The typical ring sizes used in the generation of tethered organoimidos are 7–8 membered metallacycles. Consequently, we sought a ring size in this regime.

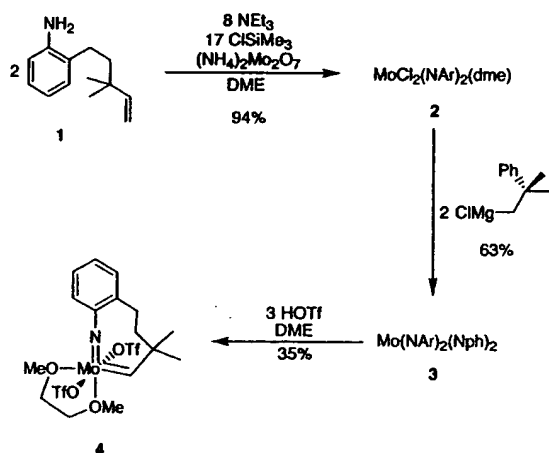
The successful strategy for the synthesis of the tethered carbene involved attachment to the *ortho*-position of an arylimido and generating an 8-membered azametallacycle. The synthesis of the aniline derivative is outlined in Scheme 1. The synthesis begins with commercially available 2-bromoethylbenzene, which is converted to the alkyl zinc by reaction with Reike zinc. Copper-mediated addition to 3,3-dimethylallyl bromide¹² occurs with the desired *S_N2'* to *S_N2* addition in a ratio of ~9 : 1 in 97% combined yield of isomers.¹³ The undesired isomer was not removed at this point, and the mixture was nitrated under standard conditions¹⁴ in high yield. The nitration occurs to generate a mixture of *ortho* and *para* isomers in a near equimolar ratio. Again, the mixture was carried forward



Scheme 1 Synthesis of 2-(3,3-dimethylpent-4-enyl)aniline (1).

without separation of isomers. Reduction of the nitro group¹⁵ provided a mixture of aniline derivatives that were readily separable by column chromatography. The final step gave 22% yield of the desired *ortho*-substituted aniline **1** based on the crude mixture of nitro isomers.

The synthetic protocol for molybdenum carbene synthesis is a modification of the literature procedure (Scheme 2).³ Reaction of **1** (H_2NAr) with NEt_3 , ClSiMe_3 , and $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ in DME provided 94% yield of $\text{Mo}(\text{NAr})_2(\text{Cl})_2(\text{DME})$ (**2**). Alkylation of **2** with 2 equiv. of neophylmagnesium chloride (NphMgCl) afforded 64% yield of $\text{Mo}(\text{Nph})_2(\text{NAr})_2$ (**3**). Addition of 3 equiv. of triflic acid in DME removes one imido ligand as the anilinium triflate and presumably generates an intermediate neophylidene bis(triflate), which was not observed. Instead, the molybdenum carbene undergoes rapid cyclization with the alkene pendant to the arylimido producing the desired tethered carbene in 35% isolated yield. Examination of the bis(triflate) by multinuclear NMR in d_5 -THF suggested 3 isomers were present in fluid solution, a complication also observed in untethered systems.⁴



Scheme 2 Synthesis of imido tethered carbene.

Bis(triflate) **4** exhibits low solubility in many common solvents. However, crystals sufficient for a preliminary X-ray diffraction study were obtained.† The isomer observed is line drawn in Scheme 2, and a structural representation from the diffraction study is shown in Fig. 2. When the structure of

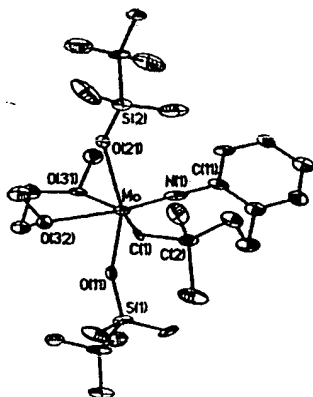


Fig. 2 Structure of **4** as found by X-ray diffraction. Selected bond distances (Å) and angles (°): Mo(1)–C(1) 1.827(19), Mo(1)–N(1) 1.723(16), Mo(1)–C(1)–C(2) 139.7(12), Mo(1)–N(1)–C(1) 173.3(14), N(1)–Mo–C(1) 101.4(7).

4 is compared to that reported for $\text{Mo}(\text{OTf})_2(\text{N}-2,6\text{-diPr}^t\text{-C}_6\text{H}_3(\text{neopentylidene}))(\text{DME})$,¹⁶ no ring strain is apparent in the metallacycle as judged by comparison of bond distances and angles.

As would be expected, the tethered carbene **4** is an active catalyst for the ROMP of norbornylene. The materials generated in those polymerizations are currently under scrutiny. Various substitution reactions on the triflate groups are being investigated as a means of synthesizing more functional metathesis catalysts.

The authors thank the Office of Naval Research, Department of Energy—Defense Programs, Petroleum Research Fund, and Michigan State University for Financial Support. JTC thanks MSU for Brubaker and Dye Fellowships.

Notes and references

† The crystals isolated were relatively weak diffractors, but a satisfactory structure was obtained. Crystal data for **4**: $\text{C}_{18}\text{H}_{25}\text{F}_6\text{MoNO}_8\text{S}_2$, $M = 657.45$, monoclinic, $a = 12.669(3)$, $b = 15.745(5)$, $c = 12.809(4)$ Å, $\beta = 92.648(6)^\circ$, $U = 2552.3(12)$ Å³, $P2(1)/c$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.764$, $T = 176(2)$ K, 11563 reflections, 3698 unique ($R_{\text{int}} = 0.2814$). The final $wR(F^2) = 0.2494$ and $R(F) = 0.1088$ for reflections $I > 2\sigma$. CCDC reference numbers 217504. See <http://www.rsc.org/suppdata/dt/b3/b311320pf> for crystallographic data in CIF or other electronic format.

- The history of olefin metathesis was recently highlighted: A. M. Rouhi, *Chem. Eng. News*, 2002, 80, 29; A. M. Rouhi, *Chem. Eng. News*, 2002, 80, 34.
- K. J. Ivin and J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, 1997.
- R. R. Schrock, *J. Am. Chem. Soc.*, 1974, 97, 6577.
- R. R. Schrock, *Chem. Rev.*, 2002, 102, 145–179.
- J. H. Oskam, H. H. Fox, K. B. Yap, D. H. McConville, R. O'Dell, B. J. Lichtenstein and R. R. Schrock, *J. Organomet. Chem.*, 1993, 459, 185.
- For examples see: J. B. Alexander, D. S. La, D. R. Cefalo, A. H. Hoveyda and R. R. Schrock, *J. Am. Chem. Soc.*, 1998, 120, 4041; D. S. La, J. B. Alexander, D. R. Cefalo, D. D. Graf, A. H. Hoveyda and R. R. Schrock, *J. Am. Chem. Soc.*, 1998, 120, 9720.
- K. C. Hultsch, J. A. Jernelius, A. H. Hoveyda and R. R. Schrock, *Angew. Chem. Int. Ed.*, 2002, 41, 589.
- A. Fürstner, H. Krause, L. Ackermann and C. W. Lehmann, *Chem. Commun.*, 2001, 2240.
- C. W. Bielawski, D. Benitez and R. H. Grubbs, *Science*, 2002, 297, 2041; C. W. Bielawski, D. Benitez and R. H. Grubbs, *J. Am. Chem. Soc.*, 2003, 125, 8424.
- For examples see: C. E. Kriley, J. L. Kerschner, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1993, 12, 2051; W.-Y. Yeh, C.-L. Ho, M. Y. Chiang and I.-T. Chen, *Organometallics*, 1997, 16, 2698; J. L. Kerschner, P. E. Fanwick and I. P. Rothwell, *J. Am. Chem. Soc.*, 1988, 110, 8235.
- For seminal examples see: U. Simeling, L. Kölling, A. Stämmler, H.-G. Stämmler, E. Kaminski and G. Fink, *Chem. Commun.*, 2000, 1177; E. A. Kretzschmar, J. Kipke and J. Sundermeyer, *Chem. Commun.*, 1999, 2381; C. Redshaw, V. C. Gibson, W. Clegg, A. J. Edwards and B. Miles, *J. Chem. Soc., Dalton Trans.*, 1997, 3343; V. C. Gibson, C. Redshaw, W. Clegg and M. R. J. Elsegood, *J. Chem. Soc., Dalton Trans.*, 1996, 4513; M. R. Lentz, P. E. Fanwick and I. P. Rothwell, *Chem. Commun.*, 2002, 2482.
- P. V. S. N. Vani, A. S. Chida, R. Srinivasan, M. Chandrasekharan and A. K. Singh, *Synth. Commun.*, 2001, 31, 219.
- L. Zhu, R. M. Wehmeyer and R. D. Rieke, *J. Org. Chem.*, 1991, 56, 1145.
- C. D. Hurd and W. W. Jenkins, *J. Org. Chem.*, 1957, 22, 1418; P. Strazzolini, A. G. Giuanini, A. Runcio and M. Scuccato, *J. Org. Chem.*, 1998, 63, 952; J. M. Mellor, S. Mittoo, R. Parkes and R. W. Millar, *Tetrahedron*, 2000, 56, 8019.
- J. J. Tepe, J. S. Madalenoitia, K. M. Slunt, K. W. Werbovetz, P. G. Spoors and T. L. Macdonald, *J. Med. Chem.*, 1996, 39, 2188; J. Razafimbelo, G. Baudouin, F. Tillequin and P. Renard, *Chem. Pharm. Bull.*, 1998, 46, 34; R. J. Fletcher, C. Lampard, J. A. Murphy and N. Lewis, *J. Chem. Soc., Perkin Trans. 1*, 1995, 623.
- R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare and M. O'Regan, *J. Am. Chem. Soc.*, 1990, 112, 3875.